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Dynamic Studies of Naphthalene Sorption on Soil from Aqueous Solution

SRI International, Menlo Park, CA

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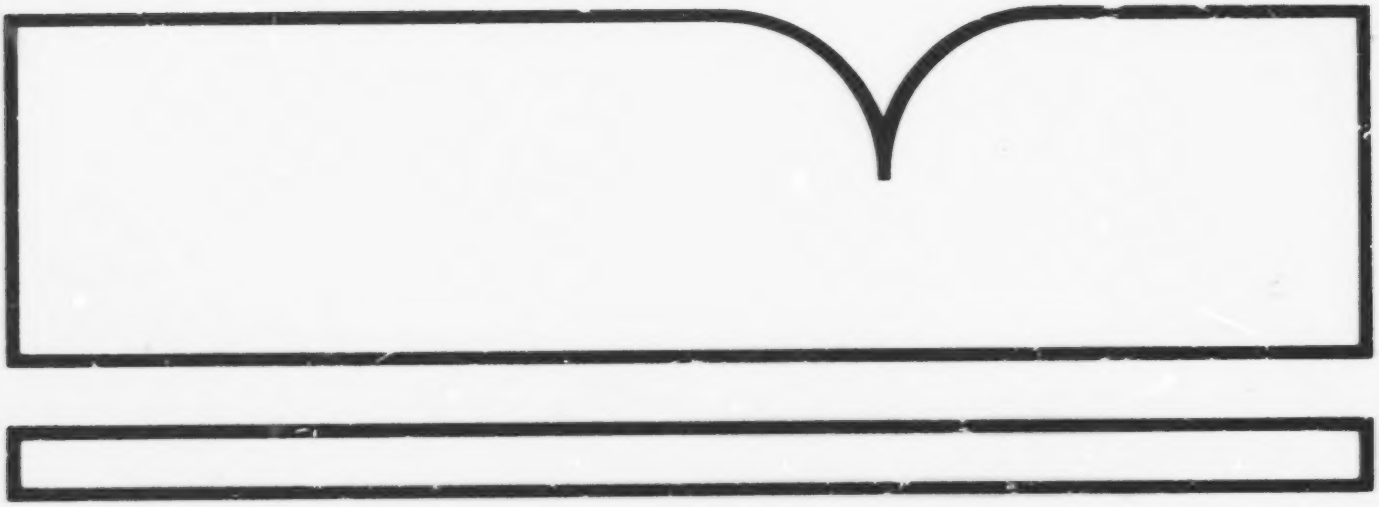

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16. ABSTRACT

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DYNAMIC STUDIES OF NAPHTHALENE SORPTION ON SOIL FROM AQUEOUS SOLUTION

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Abstract

The thermodynamics and kinetics of naphthalene sorption from water on soil were examined over the temperature range of 15°C to 50°C.

Introduction

The hydrophobic sorption model (1) has been widely used for predicting K_p values for low aqueous solubility organics, simply from the organic carbon content of the soil and the aqueous solubility of the solute. According to this model adsorption is fast and reversible and occurs principally on the organic fraction of the soil; the temperature dependence of adsorption is governed by bulk phase thermodynamics. The assumptions of fast equilibrium (2) and sorption reversibility (3,4) have been questioned recently. Little attention has been given to the thermodynamics of adsorption.

To test the hydrophobic model and to better understand adsorption thermodynamics and kinetics, we conducted flow sorption equilibrium and kinetic experiments over a range of temperatures for naphthalene sorption from water. Naphthalene was chosen because its aqueous solubility has been measured accurately over an appropriate range of temperatures (5), and thus adsorption thermodynamics can be better understood. Flow sorption methods were developed for examining the temperature dependence and reversibility of sorption. A gas purge desorption technique was used to examine desorption kinetics. These methods are described below.

Experimental Details and Methods

Materials

Two soils and one sediment were used for the naphthalene sorption studies. Menlo Park soil is a locally obtained surface soil with an organic carbon content of 1.6 ± 0.2% [deter-

mined by the Walkley-Black method (6)]. The soil pH is 5.7. Eustis sand was supplied by the U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory. The Eustis soil is a fine sand with an organic carbon content of 0.42 ± 0.03%. The major clay mineral is quartz, and the soil has a cation exchange capacity of 1.8 meq/100 g and a pH of 5.1.

EPA-6 sediment was supplied by the U.S. Environmental Protection Agency, Athens, Georgia. This sediment has an organic carbon content of 0.72, a high expandable clay content (61%) and cation exchange capacity (33.0 meq/100 g), and a pH of 8.2.

Naphthalene was obtained from Fluka Chemical Co. with a stated purity of >99%. Toluene (Mallinckrodt) was also used to test the continuous flow sorption method.

Batch Sorption Method

Soil samples were equilibrated for a minimum of 5 days in a solution of 0.01 M $CaSO_4$. Slurry samples were weighed into 25-mL centrifuge tubes. The amount of soil was varied so that C (final)/C (initial), where C is the solution concentration, would be 0.4 to 0.6. An aliquot of naphthalene in 0.01 M $CaSO_4$ solution (generally 10 to 30 mg/L) was added to the tubes, and the tubes were rotated end-over-end in a thermostatted temperature box at 25 ± 0.1°C for the required equilibration time. Blank samples of organic solution with no sorbent and sorbent with $CaSO_4$ solution were treated identically.

The tubes were centrifuged to separate the aqueous and solid phases. The aqueous supernatant was then analyzed by UV spectroscopy. The solid phase was either extracted and analyzed or the amount of chemical sorbed was calculated from the change in concentration of the supernatant solution. Analysis of the blanks determined the amount of organic chemical lost by volatilization or sorption on the glass. This amount was usually negligible.

Flow Sorption Methods

Frontal analysis has been used to measure adsorption from solution on solids for many years. Gluckauf (7) showed in 1945 that if local equilibrium is maintained at every point in a sorbent column, then an entire isotherm, up to the influent concentration of the adsorbate, could be obtained from a single experiment by integration of the breakthrough curve and knowledge of the dead volume of the column. The assumption of local sorption equilibrium is often poor, however. Sharma and Fort (8) showed that frontal analysis could be very accurate if the amount sorbed is calculated by integrating the entire breakthrough curve between known equilibrium concentrations. Because the elution curve is integrated between two equilibrium states (pure solvent and the influent solution concentration C_o), correction for non-equilibrium spreading is unnecessary. However, the adsorption isotherm must be built up from successive runs at varying C_o. If sorption is reversible, the same adsorbent column can be used for all the measurements.

Continuous flow experiments with soil columns have been used principally to study mass transfer through the columns rather than to measure adsorption isotherms (9,10). Adsorption isotherms are typically measured independently using batch methods, and these equilibrium data

are then used in column studies to deduce mass transfer information about dispersion and sorption. Several papers have appeared over the past 15 years describing frontal analysis methods for measuring adsorption (11,12), but use of these and similar methods is rare.

The method used in this study is similar to that described by Sharma and Fort (8) but adds a significant capability to the method. Adsorption is initially measured using frontal analysis and integrating the breakthrough curve to obtain the equilibrium amount adsorbed at the influent concentration. Incremental adsorption or desorption is then induced by stopping the flow and changing the temperature of the flow column. Incremental amounts sorbed can be measured very precisely by this temperature-jump method because the sorption peak is integrated above a known influent baseline and dead volume corrections are not needed.

Several other cycling schemes are possible in addition to the one described above because sorption can be induced by changing the influent concentration or by changing the temperature. The simplest scheme is to examine the adsorption/desorption at one temperature. If the four-way valve is repeatedly switched from solvent to solution and back again, then the reproducibility and extent of irreversible sorption can be examined.

The continuous flow apparatus shown in Figure 1 is essentially a high performance liquid chromatograph. Two high pressure syringe pumps (ISCO Model 314) serve as solvent reservoirs: one pump is for solute-free solvent to establish a baseline level and for desorption, and the second pump is for a solution of the solute to be studied. The flow from the two pumps is channeled to a four-way valve that is connected by stainless steel tubing to the column and to a waste receptacle. The column consists of a weighed amount of soil or sorbent material loosely packed in a short (2- to 6-inch) stainless steel tube with a 4.8-mm I.D. A 10-μm stainless steel frit on the outlet end of the column prevents loss of sorbent from the column. The column is immersed in a constant temperature bath to maintain thermal equilibrium.

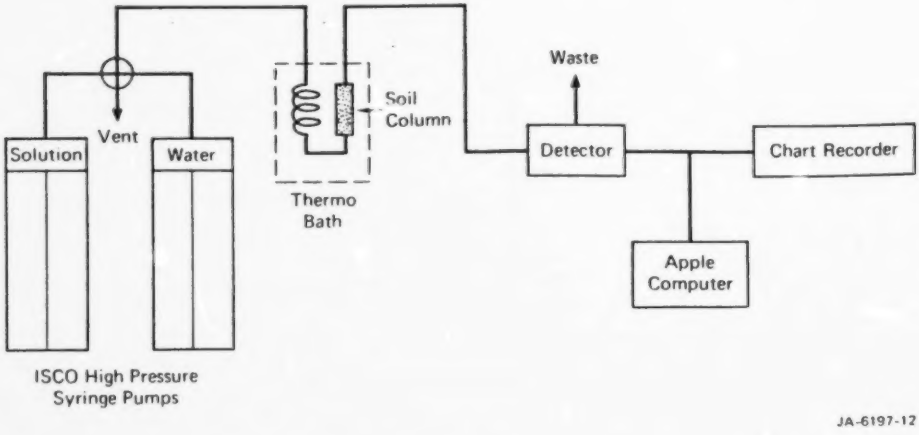

Figure 1. Continuous flow frontal analysis apparatus.

The column effluent passes through an ultraviolet absorbance detector (Waters Associates Model 440) or other appropriate continuous detector and then to a waste receptacle. The effluent can be collected in discrete fractions for other types of analytical characterization if desired. The electronic output from the detector is connected to both a strip-chart recorder for an immediate hard-copy examination of the experimental data and to an analog-to-digital (A/D) converter (Interactive Microware, Inc., ADALAB interface board) for data acquisition by minicomputer (Apple II+). The collected data can then be edited, integrated, and plotted by using a software program developed by Steven Leach of SRI International.

Gas Purge Desorption Method

Desorption rates were measured by the gaseous purge method developed by Karickhoff (2). The desorption kinetics were followed by continuously sparging the solute from the soil suspensions and collecting the vapor on Tenax traps. The initial purge interval removes the aqueous phase chemical and labile fraction of the sorbed chemical. Naphthalene was convenient to study because its high Henry's constant allows a fast purge of the solution phase. The nonlabile fraction is removed at longer purge times.

Our experimental apparatus is shown in Figure 2. To minimize sample handling and volatilization losses, approximately 1 g of prewetted soil was weighed directly into the purge vessel. Then 20 mL of a naphthalene solution was added, and the vessel was sealed with a Teflon O-ring and glass cap. The soil suspension was equilibrated in a constant temperature bath for the prescribed incubation period. An aliquot of the initial solution was extracted with hexane and analyzed by GC to determine the starting concentration. The initial solute concentration on the soil was calculated from the independently determined adsorption isotherm.

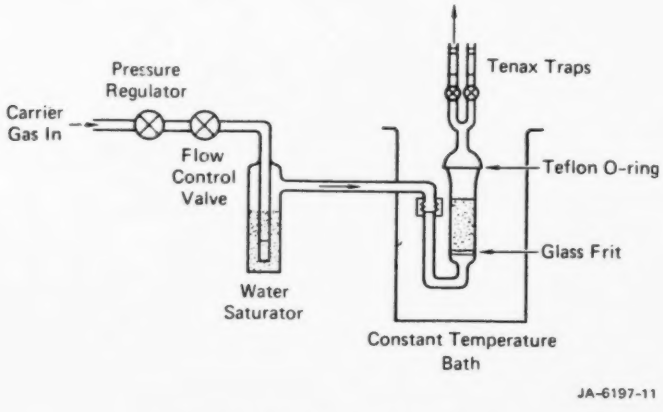

Figure 2. Desorption purge apparatus.

The naphthalene was sparged from solution with nitrogen at a constant flow rate and collected on Tenax traps. The collection intervals varied from 10 to 30 min, depending on the

amount of chemical being purged from the solution. The Tenax traps were desorbed with hexane and analyzed by GC. At the end of the purge time (>85% recovered), a 5-mL aliquot of hexane was added to the soil suspension and sonicated for 5 min. The residual sorbed chemical was extracted into the hexane.

Blank runs with no sorbent at 400 mL/min nitrogen flow showed that 95% of the aqueous-phase naphthalene was removed in the first 10 min. The total amount desorbed at each time interval was calculated as the sum of the amounts desorbed at each interval. The amount remaining on the soil was calculated by difference. At the end of the experiments mass balances were >95%.

Results and Discussion

Naphthalene Sorption Isotherms

Flow sorption experiments were performed to measure the thermal dependence and reversibility of naphthalene sorption on Menlo Park soil and Eustis sand. Influent naphthalene concentration ranged from 1.2 to 19.0 mg/L for Menlo Park soil and 4.2 to 18.3 mg/L for Eustis sand. The flow measurements were performed at 50°C, 35°C, 25°C, and 15°C.

Equilibrium batch measurements of naphthalene on both soils were obtained at room temperature for comparison with the flow sorption experiments. Menlo Park soil in amounts ranging from 36 to 1800 mg (soil loadings of 1.2 to 50 g/L) were mixed with 35 mg naphthalene/L for 48 hr. The soil was extracted with methylene chloride for analysis. Eustis sand (0.7 to 12.5 g, soil loadings of 23.5 to 490 g/L) and naphthalene in concentrations of 14 to 33 mg/L were mixed for 4 days. The soil was extracted with methanol.

The results of the naphthalene flow and batch sorption experiments are shown in Figure 3. Note first that the batch and flow data are coincidental within experimental uncertainty for the 25°C experiments for both soils. The data for the Menlo Park soil also indicate that the sorption isotherms are linear over a broad range of temperatures and concentrations. (The solubility of naphthalene is 32 mg/L at 25°C.) The K_p value calculated for the Menlo Park soil at 25°C is 23 mL/g, which results in a calculated K_{oc} = 1400. The K_p and K_{oc} values calculated for the Eustis sand isotherm at 25°C are 2.4 and 570, respectively.

The lower value of K_{oc} for the Eustis sand could be the result of its lower specific surface area or of the composition of its organic matter. To test the relative importance of surface area and type of organic matter on adsorption, we conducted batch adsorption measurements on modified and unmodified EPA-6 sediment. EPA-6 sediment was chosen for study because it has a high ratio of expandable clay to organic carbon and therefore provides an excellent substrate for modification by cationic surfactants. The sediment was modified by sorption of 85 mg/g of poly(N,N-dimethylaminoethyl methacrylate) (PDAM). This cationic oligomer adsorbs irreversibly on opposite walls of the interlamellar spaces of EPA-6 sediment with its tertiary nitrogen attached to the mineral surface and its hydrocarbon backbone exposed to the interlamellar solution phase (13).

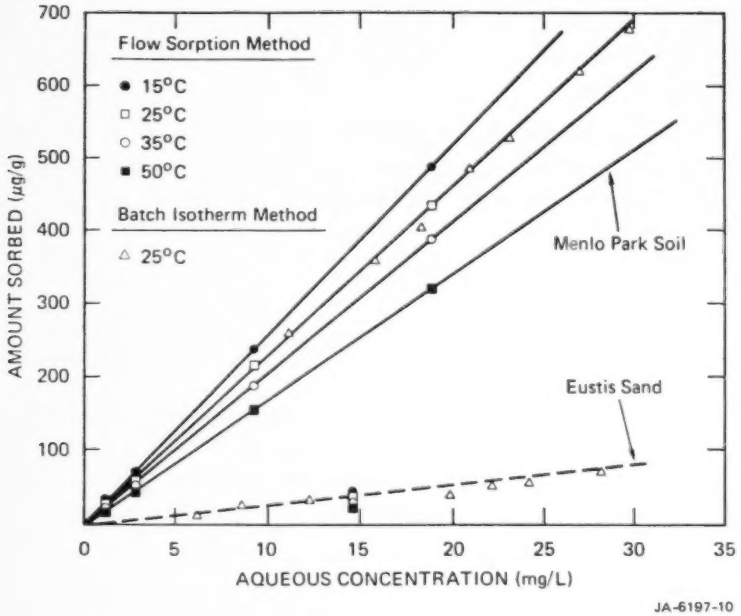

Figure 3. Thermal dependance naphthalene sorption of soil.

As shown in Figure 4 preadsorption of PDAM increased K_p values of naphthalene from 3.35 to 56 ml/g, an increase of about a factor of 17. K_{oc} values were 940 for the modified sediment and 465 for the unmodified sediment. These K_{oc} values suggest that the organic matter associated with the adsorbed PDAM interacts more strongly with naphthalene than the organic matter indigenous to the sediment. Note that PDAM has a high carbon-to-oxygen ratio of 4-to-1 and that Garbarini and Lion (14) have reported that K_{oc} values increase as the carbon-to-oxygen ratio of the organic matter increases.

These data also clearly indicate that hydrophobic sorption on clay mineral surfaces is low because of preferential adsorption of water. It is likely that the difference in K_{oc} values for the two soils (1400 versus 570 ml/g) was principally due to differences in the type of organic matter rather than to differences in clay content and surface area of the soils.

Thermodynamics of Naphthalene Sorption

To better understand the significance of calculated thermodynamic parameters of adsorption it is useful to establish an interfacial model. The model described below is based on a physical picture of soil particles suspended in an aqueous solution of organic solute, where at equilibrium the solute concentration is constant and uniform in the well-mixed bulk phase, but increases near the water/soil interface because of preferential adsorption of the solute. The soil surface is assumed to be homogeneous with respect to interactions with nonpolar

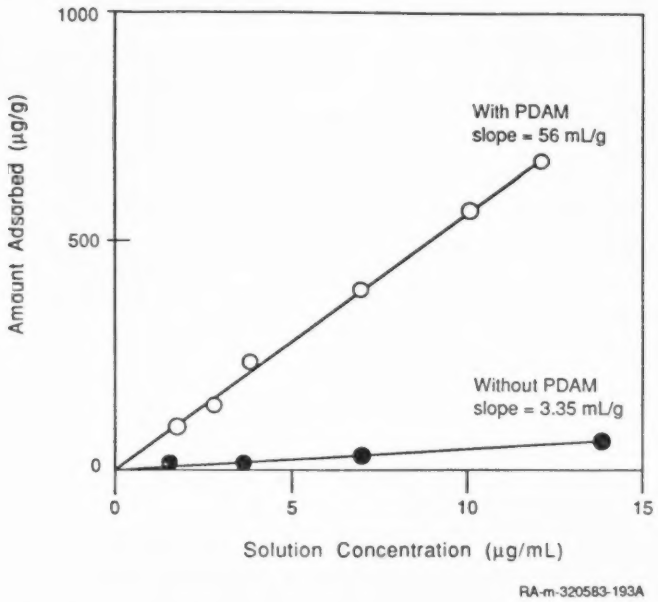

Figure. 4. Adsorption of naphthalene on EPA-6 sediment with and without preadsorped PDAM (85 mg/g sediment).

Source: Reference 13.

organics because of evidence that sorption of these materials occurs predominantly on the organic matter of soil and because the sorption isotherms of these materials are linear. The interfacial region, where the concentration of solute increases, is assumed to have a thickness of molecular dimensions because the force field of any surface does not extend more than a few monomolecular layers of water, due to the high dielectric constant of water.

Note that Chiou and co-workers (15,16) have argued that organic sorption from water on soil is not adsorption but dissolution of the organic in the organic polymer matrix attached to soil minerals. They base their arguments on the observed linearity of the isotherms (up to near saturation concentrations), the correlation of the sorption partition coefficient with the octanol water partition coefficient of the chemical, and the low temperature dependence of sorption. However these sorption characteristics can be equally well explained by an adsorption mechanism, as shown below for naphthalene sorption.

Adsorption Model

Assume a two-phase model for a soil/solution system in which the solution is divided into an adsorbed (σ) phase and a bulk liquid (ℓ) phase. The equilibrium constant for 1 mole of solute (2) replacing r moles of solvent (1) on the soil surface

$$r(1)^{\sigma} + (2)^{\ell} \rightarrow r(1)^{\ell} + (2)^{\sigma} \tag{1}$$

is given by:

$$K = \frac{x_2^{\sigma}\,\gamma_2^{\sigma}}{x_2^{\ell}\,\gamma_2^{\ell}} \left(\frac{x_1^{\ell}\,\gamma_1^{\ell}}{x_1^{\sigma}\,\gamma_1^{\sigma}} \right)^{r} \tag{2}$$

where x_1^j and γ_1^j are mole fractions and activity coefficients, respectively. For very dilute solutions, if the standard states

$$\begin{aligned} \gamma_1^{\ell} &\rightarrow 1 \quad \text{as} \quad x_1^{\ell} \rightarrow 1 \\ \gamma_1^{\sigma} &\rightarrow 1 \quad \text{as} \quad x_1^{\sigma} \rightarrow 1 \end{aligned} \tag{3}$$

are chosen, then

$$K = \frac{x_2^{\sigma}\,\gamma_2^{\sigma}}{x_2^{\ell}\,\gamma_2^{\ell}} = \exp\left[\frac{\left(\sigma^{o} - \sigma_2^{o}\right) a_2}{RT} \right] \tag{4}$$

where a_2 is the partial molar area of 2 in the surface phase, and σ_1^o and σ_2^o are the interfacial tensions of the solid/pure 1 and solid/pure 2 interfaces, respectively. Note that the solute (component 2) preferentially adsorbs ($K > 1$) when the solid/liquid free energy decreases with displacement of water by the organic solute at the interface; that is, when $\sigma_1^o > \sigma_2^o$.

The relationship between K and the measured partition coefficient K_p is given by:

$$K = \frac{K_p\,\gamma_2^{\sigma}}{v^{\sigma}\,\gamma_2^{\ell}} \tag{5}$$

where v^{σ} is the volume of the adsorbed phase per gram of soil. Thus the calculation of K depends on the estimation of γ_2^{σ} and v^{σ}.

The surface phase activity coefficient γ_2^{σ} is usually assumed to equal one or to equal the bulk phase activity coefficient. The assumption that $\gamma_2^{\sigma} = 1$ is most reasonable for completely miscible and near ideal bulk solutions. However, for a non-ideal solution of limited miscibility, such as naphthalene in water, it is more reasonable to assume that $\gamma_2^{\sigma} = \gamma_2^{\ell}$ in the dilute, Henry's law region.

The volume of the adsorbed phase is usually estimated by measuring the specific surface area of the solid and assuming a thickness (commonly one molecular layer) for the adsorbed phase. The volume of the adsorbed phase for Menlo Park soil was estimated in a more direct manner, using vapor sorption data, as described below.

Ethylbenzene vapor adsorption is very strong on dry Menlo Park soil, but decreases rapidly as soil water content increases up to about 40 mg of water per gram of soil (17). At higher water contents, vapor sorption is low and is not a strong function of soil water content. These data are consistent with data reported by Call (18) and Chiou and Shoup (19) for water and organic vapor sorption on other soils and indicate that the force field exerted by the soil surface extends to about 40 mg or 40 μL of water per gram of Menlo Park soil. This

is equivalent to about four molecular layers of water, as estimated from the water vapor adsorption isotherm (Type II according to Brunauer's classification).

Assuming that the volume of the adsorbed phase is 40 μL/g soil for Menlo Park soil, the highest amounts of naphthalene adsorbed in our experiments would give surface-phase mole fractions of less than about 0.002. It is thus not surprising that naphthalene adsorption isotherms are linear, given this very low surface coverage. Moreover, recalling that K_p is in units of mL/g soil, it is easily shown that

$$\begin{aligned} K &= K_p(mL/g)/0.040(mL/g) \\ &= 25\ K_p \end{aligned} \tag{6}$$

Standard free energy changes, calculated from experimental data using

$$\Delta G_d = -RT\ \ln K = -RT\ \ln\left(25K_p\right) \tag{7}$$

are listed in Table I.

Table I

CALCULATED THERMODYNAMIC VALUES FOR THE ADSORPTION OF NAPHTHALENE ON MENLO PARK SOIL

T (°C)	K	ΔG_d (kcal/mol)	ΔH_d (kcal/mol)	ΔS_d (eu)	ΔH_σ (kcal/mol)	ΔS_σ (eu)
15	650	-3.71	-2.1	5.6	-0.3	-10
25	575	-3.76	-2.3	4.9	-0.5	-11
35	500	-3.80	-2.8	3.2	-1.0	-13
50	400	-3.85	-2.9	2.9	-1.1	--

The enthalpy change for the surface reaction shown in equation (1) can be written as

$$\Delta H_d = \left(H_2^\sigma - H_2^\ell\right) - r\left(H_1^\sigma - H_1^\ell\right) \tag{8}$$

where ΔH_d is the enthalpy of displacement of r moles of solvent by one mole of solute and H_i^σ and H_i^ℓ are partial molar enthalpies of component i in the adsorbed and liquid phases, respectively. Equation (8) can be rewritten as

$$\Delta H_d = \Delta H_\sigma - \Delta H_\ell \tag{9}$$

where ΔH_ℓ is the bulk liquid heat of solution of liquid solute and ΔH_σ is the corresponding heat of solution in the adsorbed phase.

For the linear adsorption isotherms determined for naphthalene adsorption

$$\frac{d \ln K_p}{d (1/T)} = - \frac{\Delta H_d}{R} \tag{10}$$

Values of ΔH_d calculated from plots of ln K_p versus 1/T are listed in Table I together with values of the standard entropy of displacement calculated from

$$\Delta S_d = \frac{\Delta H_d - \Delta G_d}{T} \tag{11}$$

The calculated enthalpies of displacement are negative and thus indicate that sorption is exothermic and entirely consistent with an adsorption mechanism. This enthalpy change, however, is probably dominated by the enthalpy of dilution of naphthalene in aqueous solution: the term $-\Delta H_\ell$ in equation (9). May and Wasik (5) reported the heat of solution of solid naphthalene is 6.3 ± 0.12 kcal/mol, based on aqueous solubility data between 5°C and 30°C. The heat of fusion of naphthalene is 4.5 kcal/mol (20) and therefore $\Delta H_\ell \sim 1.8$ kcal/mol between 5°C and 30°C. Values of ΔH_σ calculated from equation (9) are listed in Table I. Note that these calculations are independent of model assumptions. These data indicate that the enthalpy of solution in the adsorbed phase is smaller and of opposite sign to the enthalpy of solution in bulk water. This suggests that displacement of water by naphthalene at the soil surface is slightly favored energetically. The apparent decrease in ΔH_σ with an increase in temperature is possibly the result of incorrectly assuming that ΔH_ℓ is constant with respect to temperature.

The entropy of displacement may also be written in a form analogous to equation (9), namely,

$$\Delta S_d = \Delta S_\sigma - \Delta S_\ell \tag{12}$$

where ΔS_σ is the entropy of solution of liquid naphthalene in the adsorbed phase and ΔS_ℓ is the corresponding entropy of solution in the bulk liquid phase. Values of ΔS_ℓ were calculated using the solubility and enthalpy of solution data of May and Wasik (5) and correcting for the entropy of fusion. Calculated values of ΔS_ℓ were approximately -16 entropy units (eu). Values of ΔS_σ were then calculated from equation (12). Note that the calculated values of ΔS_σ are negative but smaller in magnitude than values of ΔS_ℓ; thus, the entropy of displacement ΔS_d is positive. The negative values of ΔS_ℓ and ΔS_d indicate that the dissolution of naphthalene in bulk or adsorbed water is accompanied by an increase in order, possibly by rearrangement of water molecules around naphthalene with a higher degree of local order, as first suggested by Frank and Evans (21) for other nonpolar organic solutes in water. This local ordering of water molecules may be partially disrupted by the presence of the solid surface, and thus ΔS_σ values are less negative than ΔS_ℓ values. These calculations and those for the enthalpy of displacement suggest that the free energy of adsorption is dominated by the free energy of dilution of the solute in the bulk phase. Octanol/water partitioning is

also dominated by the free energy of dilution in bulk water and therefore it is not surprising that K_p and octanol/water partition coefficients show a good correlation.

It is illustrative to compare this thermodynamic analysis with that of Wauchope, Savage, and Koskinen (22), who measured naphthalene adsorption on Bosket loam soil (F_{oc} = 0.006) at 6.5°, 15°, 25°, and 37°C. Adsorption was measured using batch methods from aqueous solutions of naphthalene with 2% methanol. Adsorption isotherms were fitted to the Freundlich equation.

Several significant differences occur between the data reported by Wauchope and co-workers and those reported here. First, all isotherms reported here for naphthalene adsorption are linear. Wauchope et al. reported that the amounts adsorbed varied with the aqueous concentration to the power of 0.81 to 0.9, calculated from four points per isotherm with bulk solution equilibrium concentrations ranging from 7 ppb up to 9 ppm. The partition coefficient measured by Wauchope et al. for the highest equilibrium concentration at 25°C is comparable to the value reported here for Eustis sand (which has an F_{oc} value comparable to that of the Bosket loam) at 25°C. Wauchope et al. argue that K_p values increase at lower concentrations because adsorption sites with higher energies are filled first. However, losses due to biodegradation were reported by Wauchope et al. at longer than 48 hours, and it is possible that unaccounted losses in the 12- to 24-hr equilibrations were magnified at low concentrations in the calculation of the amount adsorbed from the change in solution concentration. Moreover, the assumption that 2% methanol in solution did not affect naphthalene adsorption may be poor, despite the report by Wauchope et al. that 2% methanol did not affect naphthalene solubility.

The possibility of experimental error or changes in adsorption caused by the presence of methanol are further suggested by the reported temperature dependence of adsorption. K_p values calculated from the data of Wauchope et al. increase with increasing temperature, in contrast to the data reported here. Values of the isosteric enthalpy of adsorption, calculated from the slope of the adsorption isotherms by Wauchope et al., are negative at the higher temperatures and positive at lower temperatures. The data reported here are unequivocable about the direction of the temperature dependence of adsorption: adsorption decreases with increasing temperature and isosteric enthalpies of adsorption are negative. The precision and consistency of the data reported here illustrate the advantages of the temperature-jump flow method for measuring the temperature dependence of sorption. It is not surprising that Wauchope et al. obtained inconsistent results considering that they were comparing small differences in the amounts adsorbed at different temperatures with different soil samples.

Desorption Rate Studies

The desorption of naphthalene from Menlo Park soil is shown in Figure 5 as a function of temperature and incubation time. Note that the naphthalene desorbs more slowly as the temperature decreases and as the incubation time increases. These data can be understood if it is assumed that the slow desorption process indicated by the data in Figure 5 is the result of diffusion of naphthalene out of the porous organic material of the soil. At high temperatures, molecular diffusion of naphthalene in pore water increases and diffusional retardation by sorption on pore walls decreases. Thus, desorption is expected to be faster at higher temperatures. Because K_p is relatively small and is only a weak function of temperature, it is

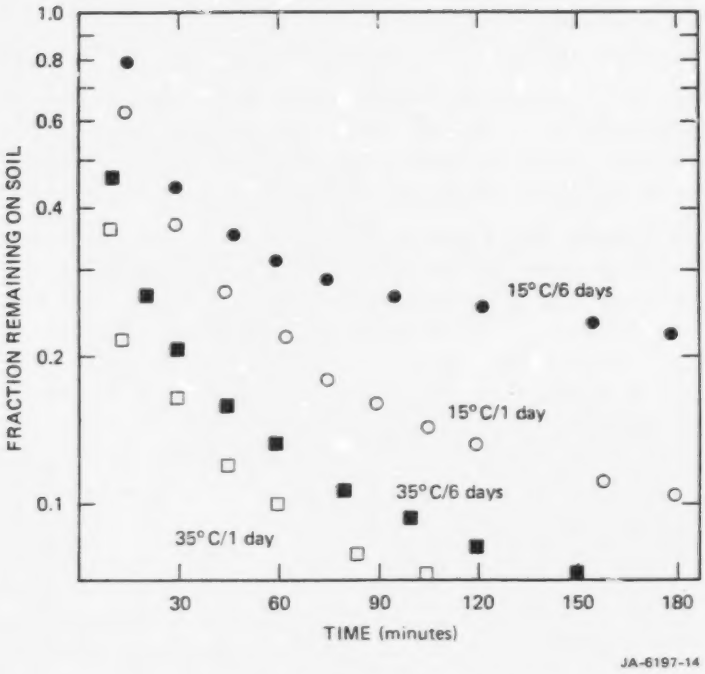

Figure 5. Desorption of naphthalene from Menlo Park soil as a function of temperature and incubation time.

likely that the predominant thermal effect on the desorption rate (at short incubation times) is an increase in the diffusion coefficient of naphthalene in pore water, D_p. If D_p is proportional to the bulk water diffusion coefficient, the value of D_p should increase by a factor of about 2-3 (23) when the temperature increases from 15°C to 35°C. Note in Figure 5 that for 1-day incubation times the time required to remove a given fraction of sorbed material at 15°C is three times longer than at 35°C.

However, at 6-day incubation times this ratio increases significantly because of the very slow desorption at 15°C. This effect may be explained as follows. The organic material has pores of varying dimensions. Diffusion of organic solutes in pores that are much larger than the molecular dimensions of the solute is similar to diffusion in bulk water, except, of course, that movement through these pores is retarded by sorption. For naphthalene sorption, retardation in the macropores is small. Diffusion in pores that approach the molecular dimensions of the solute can, however, be significantly retarded.

Diffusion in micropores is retarded by increased frictional drag on the solute from fine pore walls (24,25) and by adsorption (26). For strongly adsorbed solutes, the diffusivity of an adsorbed solute is retarded by a factor of $1/K_p$ relative to an equivalent-sized nonadsorbed

solute if the adsorbed solute is immobile. Moreover, K_p values may increase as the pore size approaches molecular dimensions because of the overlap of force fields from pore walls surrounding a sorbed molecule. Peel and co-workers (27) have developed a branched pore kinetic model for activated carbon adsorption in which separate diffusion coefficients and equilibrium adsorption parameters are used for macropores and micropores.

This physical picture of sorption indicates that at least three steps are involved in the approach to sorption equilibrium: (1) diffusion in bulk water to the external soil surface; (2) intraparticle molecular diffusion in the macropores of the organic carbon; and (3) intraparticle molecular diffusion in micropores of the organic carbon. Sorption equilibrium constants should be approximately equal on the external and macropore surfaces, but should be significantly greater within micropores. In a well-agitated system, sorption equilibrium with the external surface should be very fast. However, intraparticle sorption kinetics are limited by retarded molecular diffusion, which becomes slower as the overall K_p value of the sorbate increases and the pore dimensions decrease.

Conclusions

The temperature-jump method is a useful modification of the frontal analysis method. Once sorption equilibrium has been established, the temperature dependence and reversibility of sorption can be measured precisely using the temperature-jump method because dead volume and blank corrections are unnecessary. The precision of the method is illustrated by the data presented in this paper on naphthalene sorption particularly when compared with similar data collected by Wauchope and co-workers using batch adsorption methods.

Thermodynamic analysis of the naphthalene/Menlo Park soil system indicates that the isosteric enthalpy of adsorption is exothermic and that the heat evolved during adsorption is probably dominated by the heat of dilution of liquid naphthalene in water. A two-phase solution model in which surface phase and bulk phase activity coefficients were assumed to be equal was used to calculate standard free energies and entropies of adsorption. Calculated free energies of adsorption showed little temperature dependence. Calculated entropies of adsorption were positive and diminished with an increase in temperature. Calculated entropies of solution in the adsorbed phase were negative but less negative than entropies of solution in bulk water, indicating that the soil surface partially disrupts the local ordering effect of water surrounding hydrophobic solutes.

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